ACS APPLIED MATERIALS & INTERFACES

Subscriber access provided by UCL Library Services

Letter

Free-Standing Photonic Crystal Films with Gradient Structural Colors

Haibo Ding, Cihui Liu, Baofen Ye, Fanfan Fu, Huan Wang, Yuanjin Zhao, and Zhongze Gu

ACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.6b01991 • Publication Date (Web): 10 Mar 2016

Downloaded from http://pubs.acs.org on March 11, 2016

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

ACS Applied Materials & Interfaces is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society.
However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Free-Standing Photonic Crystal Films with Gradient Structural Colors

Haibo Ding,[§] Cihui Liu,[§] Baofen Ye, Fanfan Fu, Huan Wang, Yuanjin Zhao, Zhongze Gu**

State Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, China;

Keywords: photonic crystal; colloidal crystal; structural color; film; angle independent

Abstract

Hydrogel colloidal crystal composite materials have a demonstrated value in responsive photonic crystals (PhCs) via controllable stimuli. Although they have been successfully exploited to generate a gradient of color distribution, the soft hydrogels have limitations in terms of stability and storage caused by dependence on environment. Here, we present a practical strategy to fabricate free-standing PhC films with a stable gradient of structural colors using binary polymer networks. A colloidal crystal hydrogel film was prepared for this purpose, with continuously varying photonic band gaps corresponding to the gradient of the press. Then, a second polymer network was used to lock the inside non-close-packed PhC structures and color distribution of the hydrogel film. It was demonstrated that our strategy could bring about a solution to the angle-dependent structural colors of the PhC films by coating the surface with special microstructures.

Photonic crystals (PhCs) have emerged as attractive optical materials for controlling and manipulating the transmission of light based on the property of photonic band gaps (PBGs). [1-3] Such materials have demonstrated their value in waveguides, [4] biosensors, [5] displays, [6] and many other optical applications. [7] Compared with top-down fabrication methods, colloidal self-assembly has been used in the fabrication of three-dimensional (3D) PhCs with low fabrication costs and mild processing conditions. [8-11] Based on this bottom-up approach, numerous studies have achieved desired structural colors by using a variety of materials. [12-14] Among these materials, the combination of highly ordered colloidal crystals and elastic hydrogels shows great potential in generating arbitrary color distribution for given materials. [15-17] Swelling or shrinking upon stimulation of these hydrogels would lead to a change in the PBGs of the colloidal crystals. [18, 19] One challenge confronting these PhC materials is to obtain films with continuously varying PBGs, which are found to be valuable for monochromators, spectrometers, and colorimetric sensors. [20] A practical strategy was proposed by treating a colloidal crystal hydrogel film with a stress gradient, leading to a gradient distribution of PBGs along the film. [21] However, this composite structure had the intrinsic defect that the hydrogel relied on its working environment. The stability of non-close-packed colloidal crystal arrays embedded in a hydrogel polymer would be easily affected by external stimuli, such as humidity and temperature. In addition, the angle dependence of the PBG had a negative effect on the PhC structures and would bring about indistinct contrasts of the generated colors. Therefore, new approaches for generating free-standing PhC films with gradients of the structural colors are still anticipated.

Here, we develop an easy method for overcoming the above drawbacks of colloidal crystal hydrogel films and demonstrate its application to fabricate free-standing PhC films with continuously varying PBGs. For this purpose, a hydrogel network was first polymerized to build stress-responsive films with photocurable silica suspension. Then, a monomer of photosensitive resin was used to replace the liquid in the hydrogel network and to lock the non-close-packed PhC structures by a second polymerization. In particular, a robust full-color film would be fabricated when the hydrogel film was under a stress gradient before the second polymerization. By combining the binary polymer networks strategy with circular symmetry microstructures on the surface of an elastic PhC film, we found the solution to the intrinsic angle dependence of the PBGs that the free-standing film with a gradient of structural colors was angle-independent around the center axis of the microstructures.

The schematic illustration of this fabrication process is outlined in **Figure 1**. In a typical experiment, a stress-responsive PhC film was fabricated by photopolymerization of the hydrogel to first lock the non-close-packed colloidal crystal arrays. A fixture was used to compress the film with a gradient of thickness. With an appropriate compression ratio, continuous distribution of structural colors could be achieved while the film recovered to the initial state after removing the fixture (**Figure 1a**). As illustrated in **Figure 1b**, the monomer of a free-standing polymer was infiltrated into the hydrogel network when the stress gradient was applied on the elastic film. With a second polymerization, the shape of the compressed film as well as the gradient colors could be preserved with the generated solid polymer network. Thus, a free-standing PhC film was imparted with continuously varying PBGs when the fixture was removed.

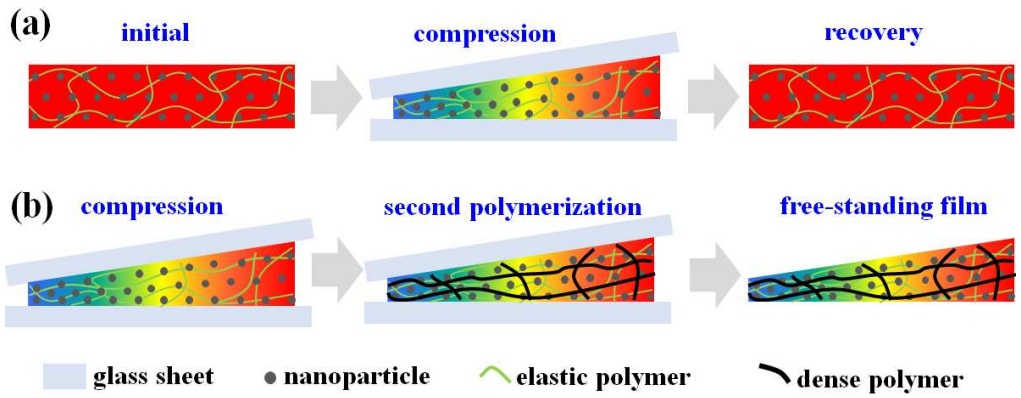

Figure 1 Comparison of PhC films with gradient structural colors for single polymer network and binary polymer networks: (a) a colloidal crystal hydrogel film was imparted with continuously varying structural colors when compressed by a fixture and returned to its initial state after removing the fixture; (b) a second polymerization was used to lock the compressed film and a free-standing film with gradient structural colors was achieved with binary polymer networks.

To fabricate stress-responsive PhC films with high quality, monodisperse silica nanoparticles were well dispersed in a pre-gel solution, following a strict ion exchange process to reduce ionic impurities. After these treatments, silica nanoparticles self-assembled into ordered and non-close-packed colloidal crystal array structures in the solution because interparticle repulsion occurred at the average interparticle spacing. The highly ordered nanoparticles imparted the pre-gel suspension with brilliant structural colors, and the color could be adjusted by using different sizes or concentrations of the silica nanoparticles. For composites composed of hydrogels and colloid crystals, the interparticle spacing can be tuned up to 2.6 times the particle size, [19] which provides the possibility of preparing a full-color pre-gel solution with the same particles. The

silica particles with a diameter of 125 nm were chosen for the preparation of the pre-gel suspension with a concentration between 0.1 to 0.3 g/mL (**Figure 2**). The digital images (**Figure 2a**) show structural colors from blue to red and the corresponding spectra (**Figure 2b**) showed a shift of the central wavelength from 495 to 645 nm. The brilliant colors could be completely preserved once the pre-gel suspension was solidified by UV light. The pre-gel solution was composed of poly(ethylene glycol) diacrylate (PEGDA), polyethylene glycol (PEG), and the photoinitiator 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP). In this solution system, PEGDA could act not only as a monomer of the hydrogel, but also as the cross-linker. PEG was blended into the solution to reduce the degree of crosslinking of PEGDA, which could make the resultant hydrogel more elastic.

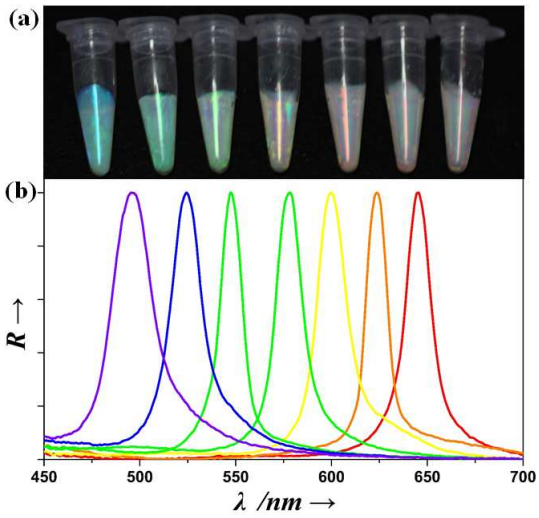

Figure 2 Photographs (a) and reflection spectra (b) of seven colloidal crystal suspensions prepared using different concentration of silica nanoparticles. From right to left, the concentrations of silica nanoparticles were 0.1, 0.13, 0.16, 0.2, 0.23, 0.27, and 0.3 g/mL.

The second polymerization was proposed to inherit the tunable property of the PEGDA hydrogel and preserve the ordered nanostructures in the free-standing states. Thus, a specialized pre-gel solution was prepared for the second polymerization that was composed of hydroxyethylmethacrylate (HEMA) as the monomer, ethylene glycol dimethacrylate (EGDMA) as the cross-linker, and HMPP as the photoinitiator. **Figure 3a** illustrates the operation sequence of the second photopolymerization. The achieved PEGDA film was immersed in absolute ethyl alcohol to replace the water. Ethanol was chosen for its intersolubility with the HEMA monomer to help the pre-gel solution infiltrate into the existing hydrogel network. After the replacement process, the PEGDA film was immersed in the pre-gel solution of the photosensitive resin and ethanol was selectively evaporated for 12 h at 60 °C. A robust film with brilliant structure color was obtained with a second UV irradiation.

The PBG position (λ) of a 3D colloidal crystal that diffracts light of a specific wavelength is determined by the Bragg's equation: [19, 22]

$$m\lambda = 1.633D\,(n_{average}^{2} - sin^{2}\theta)^{1/2}, \qquad (1)$$

where m is the order of diffraction, D is the center-to-center distance between nearest particles, $n_{average}$ is the average refractive index of the system composed of colloids and surroundings, and θ is the glancing angle between the incident light and the sample normal. Based on Equation (1), the replacement of liquid in the hydrogel matrix would result in the change of D and $n_{average}$, leading to a shift of λ. The photographs and spectra during the process of the second polymerization are shown in **Figure 3b** and **3c**. In the first step, the introduction of ethanol brought about a shrinkage of the PEGDA network, leading to a decrease in the interplanar distance. Despite the increase in $n_{average}$ ($n_{ethanol}$ = 1.36, n_{water} = 1.333), both the corresponding λ recorded by the spectrometer and the structure color observed by the naked eye showed a blue-

shift , which meant that the hydrogel shrinkage had a more decisive effect on the PBG than that of the change of average refractive index. Then, the HEMA monomer could recover the shrinkage in PEGDA network along with an even higher refractive index (n_{HEMA} = 1.4505). Interestingly, the film became transparent when immersion in the HEMA monomer occurred, because for the closer difference in refractive index between the colloids and the surroundings. It could be also concluded that there were air voids within the robust film from the increase in the reflected intensity and the minor blue-shift of the central wavelength. [23, 24] The air voids were caused by the evaporation of remaining water or ethanol in the PEGDA network, which could never be eliminated during the replacement process.

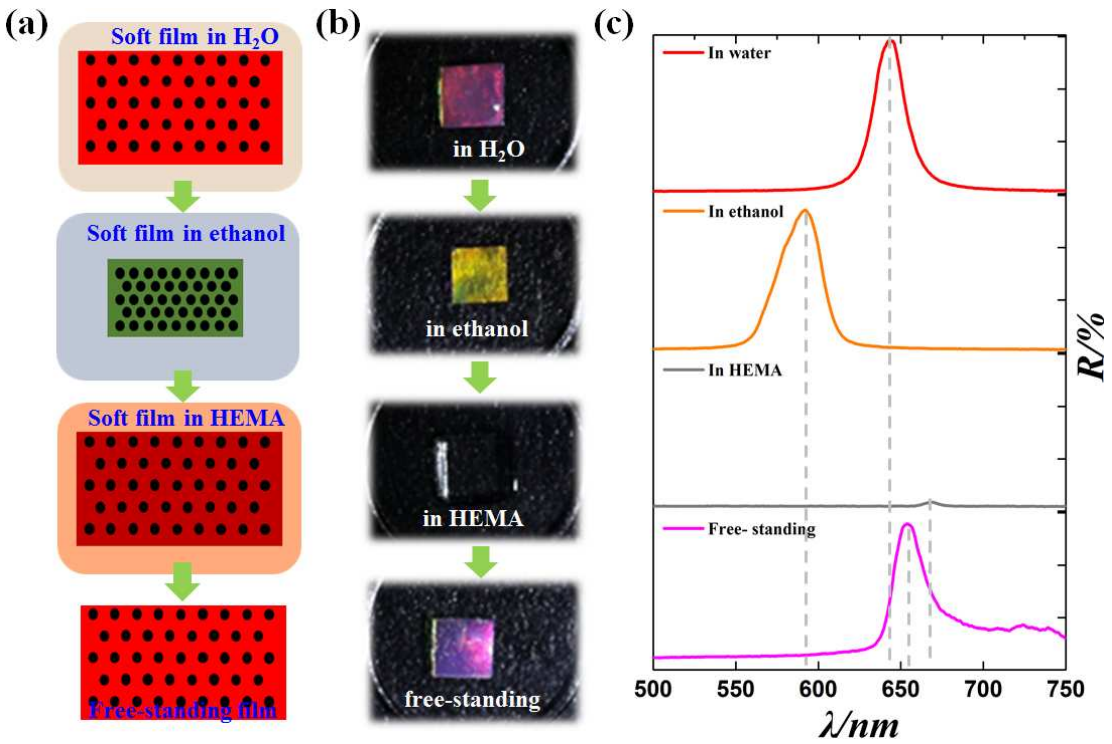

Figure 3 (a) Schematic illustration of the colloidal crystal arrays locked in the polymer network during the fabrication process. (b) Photographs and (c) reflection spectra of the PhC films during the fabrication process.

With the second polymerization of HEMA, the PEGDA hydrogel network and the embedded silica nanoparticles could be sustained by the addition of the robust polymer network. Consequently, it is possible to lock the compressed state of the elastic hydrogel film by the same method. We used the mechanical pressure to vary the thickness of the film and to tune the PBGs of the films. The thickness was equal to $d_{111} \times M$ (where d_{111} is the interplanar distance of the (111) diffracting planes and M is the total number of layers of the colloidal crystal (111) diffraction plane). When the film was subjected to compression, the thickness decreased and M was kept constant, leading to a decreasing d_{111}. Bragg's equation can be approximately expressed in Equation (2) by considering the interplanar distance of the (111) diffracting planes:

$$m\lambda = 2\, d_{111}\, (n_{average}^{2} - sin^{2}\theta)^{1/2}. \qquad (2)$$

In a certain range, different compression of the film's thickness could cause a proportional decreasing percentage of λ. [21, 25] To fabricate a robust PhC film with a gradient of structural colors, the additional step in the fabrication of robust films was a specialized fixture to compress the film before the second polymerization (**Figure 1b**). Our previous work discussed how to control the working range of the film, [21] and the operating factors in the fabricating process are described in detail in the Methods section. Thus, the free-standing film with a continuous PBG could be preserved without the fixtures and the water environment (**Figure 4a** and **4b**). In previous work, it was considered that the PEGDA network locked the ordered nanostructures of the colloidal crystal arrays. [21, 25, 26] However, the non-close-packed structures have not been characterized by scanning electron microscopy (SEM) images for the reserved liquids in the hydrogel network. The addition of a solid polymer network provided a possibility of observing

the microstructures of the PhC film by SEM. The images were captured at different places along the gradient direction. From the cross-sectional images (**Figure 4c–f**), it can be seen that the distance between two neighboring particles decreased with the reduction in the film thickness, which meant a decrease in the (111) interplanar spacing along the direction of increasing stress and the corresponding PBG reduced. Moreover, it can be observed that the monodisperse silica nanoparticles on the film surface form a predominantly hexagonal symmetry (**Figure S1**). Compared with the cross section, the compression along the film seemed to have no effect on the distance between neighboring particles.

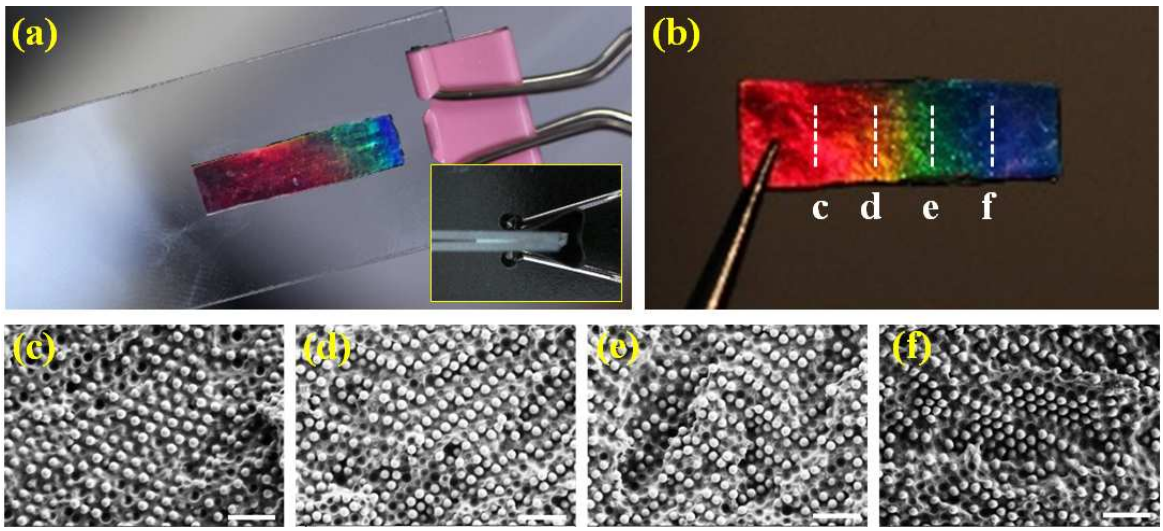

Figure 4. (a) Photograph of the film and the fixture after the second polymerization. (b) Photograph of a free-standing PhC film with gradient structural colors. (c-f) Cross-sectional SEM characterizations of the gradient structural color film at positions indicated by the dashed lines in Figure 4 (b). Scale bars are 1 μm.

Free-standing films with iridescent colors covering the whole visible range have been fabricated according to the above methods. The structural colors and the reflection spectra at different positions of the generated robust films are given in **Figure 5a**. The film showed a

gradual change in the reflection color from red to blue; the central wavelength of the PBG started from an initial wavelength of 618.4 nm and ended with a shorter wavelength of 514.2 nm. The spectra were collected at local areas of round dots of 300 μm diameter at intervals of 0.25 mm along the film. From the PBG position shown in **Figure 5b**, the relationship between the PBG position and the spatial position along the compression direction was not linear as expected. The main reason for this were considered to be the limited compression ratio of the hydrogel materials and the deformation of the glass fixtures for compression. In our experiment, the full width at half maximum (FWHM) of the PBG stayed at around 20 nm over the whole range, indicating the improvement in the refractive index contrast between the materials based on the addition of HEMA polymer. [27]

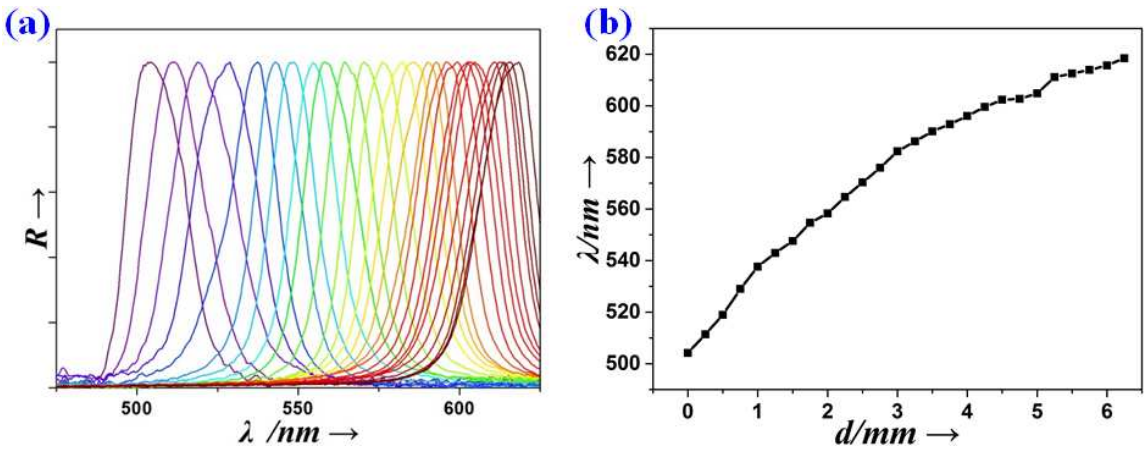

Figure 5 (a) The corresponding reflectance spectra (normalized) of the selected film at intervals of 0.25 mm along the gradient direction. (b) The relationship between the reflectance peaks and the position.

In principle, because of the effect of Bragg diffraction, the PhC films show angle-dependent structural colors at different viewing angles, which is disadvantageous for the construction of display devices. Inspired by natural creatures, researchers have made progress in developing

noniridescent structural colors with amorphous PhCs [28] and angle-independent PhCs by using colloidal crystal fibers or colloidal crystal beads as elements of the materials. [29, 30] The colloidal crystal fibers showed identical reflective color only when observed perpendicular to the axial direction of the fibers, while the colloidal crystal beads showed identical structure colors independent of the rotation of the axes for their spherical symmetry. [29] Here, we present desired PhC films with the feature of anisotropic angle independence by fabricating circular symmetry microstructures on the surface. Templates of aligned glass fibers (100 μm in diameter) were first prepared (**Figure 6a**). Then, polydimethylsiloxane (PDMS) polymers were used to replicate the circular symmetry microstructures, which acted as the antitemplate for PhC films. A colloidal crystal hydrogel film was fabricated based on the PDMS template. Both the structural colors and the circular symmetry microstructures remained after the second polymerization. Characteristic photographs of the fabrication process are recorded in **Figure 6b–d**. When the films with circular symmetry microstructures were combined with a continuously varying PBG distribution, the microstructures could remain under compression. Note that the pre-gel solution for the second polymerization not only infiltrated into the photonic crystal film but also filled up the valleys of the curved surface, leading to a flat surface (**Figure S3**). The films showed observable and angle-independent structural colors perpendicular to the axial direction of the microstructures (**Figure 6e**). The spectra present the difference between the films with or without circular symmetry microstructures on surfaces when observing at different angles (**Figure 6f** and **g**). The films with the microstructures showed structural colors with the property of angle independence when observed perpendicular to the axial direction of the microstructures. The relationships between the PBGs and the viewing angles have proved to conform to the designed plan.

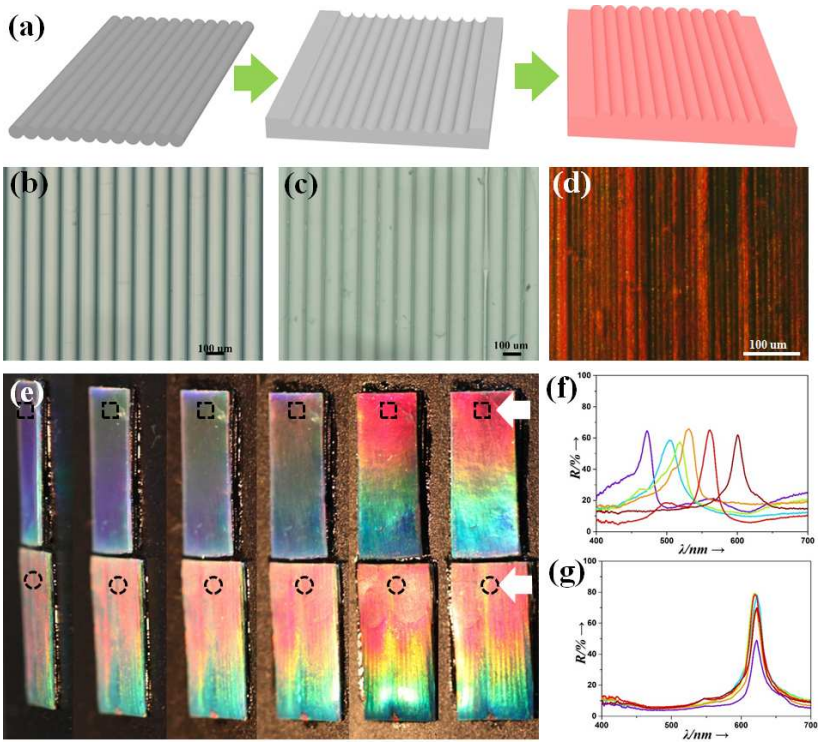

Figure 6 (a) Schematic illustration of the fabrication of PhC films with circular symmetry microstructures. (b-d) Optical images of (b) the template made of glass fibers, (c) PDMS antitemplate, and (d) PhC films with circular symmetry microstructures on its surface. (e) Photographs of the films with a continuous color distribution observed at different viewing angles. The above film is flat while the below one is coated with circular symmetry microstructures. (f, g) Reflection spectra collected at different viewing angles for (f) the flat PhC film and (g) the PhC film with circular symmetry microstructures on its surface. Comparable with the flat film, the film with circular structures is thick, thus its reflection has a little higher intensity. The reflectance intensity of the photonic crystal film with circular structures reduced due to the enhancement of the light scattering when the detection angle was increased.

In conclusion, we have demonstrated a practical strategy for the construction of free-standing PhC films with gradient structural colors based on stress-responsive colloidal crystals and binary polymer networks. The PBGs of the PhC films could be tuned by a gradient distribution of compression, which could be locked by another polymer network upon a second polymerization. By combining the achieved film with special color distribution and circular symmetry microstructures on the surfaces, we have demonstrated a robust PhC film with angle-independent structural color perpendicular to the axial direction of the microstructures. As our strategy was able to overcome the storage demand for PhC materials, it is expected that they could be integrated into other optical instruments and displays.

Supporting Information Available

Experimental procedure details; Scanning electron microscopy images. This material is available free of charge via the Internet at http://pubs.acs.org.

Corresponding Author

gu@seu.edu.cn; yjzhao@seu.edu.cn

Author Contributions

[§]H.D. and C.L. contributed equally to this work.

Notes

The authors declare no competing financial interests.

Acknowledgement

This work was supported by the National Science Foundation of China (Grant Nos. 21473029 and 51522302), the NSAF Foundation of China (Grant No. U1530260), the National Science Foundation of Jiangsu (Grant No. BK20140028), the Research Fund for the Doctoral Program of Higher Education of China (20120092130006), the Program for New Century Excellent Talents in University, the Research Innovation Program for College Graduates of Jiangsu Province (KYLX_0189), and the Scientific Research Foundation of Southeast University.

References

(1) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. Photonic Crystals: Putting a New Twist on Light. *Nature* **1997**, *386*, 143–149.

(2) Noda, S.; Tomoda, K.; Yamamoto, N.; Chutinan, A. Full Three-Dimensional Photonic Bandgap Crystals at Near-Infrared Wavelengths. *Science* **2000**, *289*, 604–606.

(3) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. Monodispersed Colloidal Spheres: Old Materials with New Applications. *Adv. Mater.* **2000**, *12*, 693–713.

(4) Russell, P. Photonic Crystal Fibers. *Science* **2003**, *299*, 358–362.

(5) Xie, Z. Y.; Cao, K. D.; Zhao, Y. J.; Bai, L.; Gu, H. C.; Xu, H.; Gu, Z. Z. An Optical Nose Chip Based on Mesoporous Colloidal Photonic Crystal Beads. *Adv. Mater.* **2014**, *26*, 2413–2418.

(6) Wu, L.; Dong, Z.; Kuang, M.; Li, Y.; Li, F.; Jiang, L.; Song, Y. Printing Patterned Fine 3D Structures by Manipulating the Three Phase Contact Line. *Adv. Funct. Mater.* **2015**, *25*, 2237–2242.

(7) Zhao, Y. J.; Xie, Z. Y.; Gu, H. C.; Zhu, C.; Gu, Z. Z. Bio-Inspired Variable Structural Color Materials. *Chem. Soc. Rev.* **2012**, *41*, 3297–3317.

(8) Gu, Z. Z.; Fujishima, A.; Sato, O. Fabrication of High-Quality Opal Films with Controllable Thickness. *Chem. Mater.* **2002**, *14*, 760–765.

(9) Wang, D.; Möhwald, H. Template-Directed Colloidal Self-Assembly – the Route to "top-

Down" Nanochemical Engineering. *J. Mater. Chem.* **2004**, *14*, 459–468.

(10) Mao, Z.; Xu, H.; Wang, D. Molecular Mimetic Self-Assembly of Colloidal Particles. *Adv. Funct. Mater.* **2010**, *20*, 1053–1074.

(11) Huang, Y.; Zhou, J.; Su, B.; Shi, L.; Wang, J.; Chen, S.; Wang, L.; Zi, J.; Song, Y.; Jiang, L. Colloidal Photonic Crystals with Narrow Stopbands Assembled from Low-Adhesive Superhydrophobic Substrates. *J. Am. Chem. Soc.* **2012**, *134*, 17053–17058.

(12) Arsenault, A. C.; Puzzo, D. P.; Manners, I.; Ozin, G. A. Photonic-Crystal Full-Colour Displays. *Nat. Photonics* **2007**, *1*, 468–472.

(13) Ge, J.; Hu, Y.; Yin, Y. Highly Tunable Superparamagnetic Colloidal Photonic Crystals. *Angew. Chem. Int. Ed.* **2007**, 46, 7428–7431.

(14) Zhang, Y.; Fu, Q.; Ge, J. Photonic Sensing of Organic Solvents through Geometric Study of Dynamic Reflection Spectrum. *Nat. Commun*. **2015**, *6*, 7510.

(15) Holtz, J. H.; Asher, S. A. Polymerized Colloidal Crystal Hydrogel Films as Intelligent Chemical Sensing Materials. *Nature* **1997**, *389*, 829–832.

(16) Ye, B. F.; Ding, H. B.; Cheng, Y.; Gu, H. C.; Zhao, Y. J.; Xie, Z. Y.; Gu, Z. Z. Photonic Crystal Microcapsules for Label-Free Multiplex Detection. *Adv. Mater.* **2014**, *26*, 3270–3274.

(17) Zhang, B.; Cheng, Y.; Wang, H.; Ye, B. F.; Shang, L. R.; Zhao, Y. J.; Gu, Z. Z. Multifunctional Inverse Opal Particles for Drug Delivery and Monitoring. *Nanoscale* **2015**, *7*, 10590–10594.

(18) Budhlall, B. M.; Marquez, M.; Velev, O. D. Microwave, Photo- and Thermally Responsive PNIPAm−Gold Nanoparticle Microgels. *Langmuir* **2008**, *24*, 11959–11966.

(19) Ge, J.; Yin, Y. Responsive Photonic Crystals. *Angew. Chem. Int. Ed.* **2011**, *50*, 1492–1522.

(20) Hou, J.; Zhang, H.; Yang, Q.; Li, M.; Song, Y.; Jiang, L. *Angew. Chem. Int. Ed.* **2014**, *53*, 5791–5795.

(21) Ding, H. B.; Liu, C. H.; Gu, H. C.; Zhao, Y. J.; Wang, B. P.; Gu, Z. Z. Responsive Colloidal Crystal for Spectrometer Grating. *ACS Photonics* **2014**, *1*, 121–126.

(22) Galisteo-López, J. F.; Ibisate, M.; Sapienza, R.; Froufe-Pérez, L. S.; Blanco, Á.; López, C. Self-Assembled Photonic Structures. *Adv. Mater.* **2011**, *23*, 30–69.

(23) Kim, S.-H.; Jeong, W. C.; Hwang, H.; Yang, S.-M. Robust Chirped Photonic Crystals Created by Controlled Colloidal Diffusion. *Angew. Chem. Int. Ed.* **2011**, *50*, 11649–11653.

(24) Ge, D.; Lee, E.; Yang, L.; Cho, Y.; Li, M.; Gianola, D. S.; Yang, S. A Robust Smart Window: Reversibly Switching from High Transparency to Angle-Independent Structural Color Display. *Adv. Mater.* **2015**, *27*, 2489–2495.

(25) Ding, H. B.; Cheng, Y.; Gu, H. C.; Zhao, Y. J.; Wang, B. P.; Gu, Z. Z. Tunable Fiber Bragg Grating Based on Responsive Photonic Crystals. *Nanoscale* **2013**, *5*, 11572–11576.

(26) Ye, B. F.; Wang, H.; Ding, H. B.; Zhao, Y. J.; Pu, Y. P.; Gu, Z. Z. Colorimetric Logic Response Based on Aptamer Functionalized Colloidal Crystal Hydrogels. *Nanoscale* **2015**, *7*, 7565–7568.

(27) Kim, S.-H.; Park, H. S.; Choi, J. H.; Shim, J. W.; Yang, S.-M. Integration of Colloidal Photonic Crystals toward Miniaturized Spectrometers. *Adv. Mater.* **2010**, *22*, 946–950.

(28) Shi, L.; Zhang, Y.; Dong, B.; Zhan, T.; Liu, X.; Zi, J. *Adv. Mater.* **2013**, *25*, 5314–5320.

(29) Gu, H. C.; Zhao, Y. J.; Cheng, Y.; Xie, Z. Y.; Rong, F.; Li, J. Q.; Wang, B. P.; Fu, D. G.; Gu, Z. Z. Tailoring Colloidal Photonic Crystals with Wide Viewing Angles. *Small* **2013**, *9*, 2266–2271.

(30) Zhao, Y. J.; Shang, L. R.; Cheng, Y.; Gu, Z. Z. Spherical Colloidal Photonic Crystals. *Acc. Chem. Res.* **2014**, *47*, 3632–3642.

Graphical Abstract or Table of Contents